#### 08-21-06 19:31 Pg: 3/28

## BEST AVAILABLE COPY

Serial No. 10/501,876

WALSDORFF et al.

NDDQ LLP

PP++53257

tion into the claim by reference to Claim 1. Entry and consideration of the attached is, therefore, respectfully solicited.

The Examiner rejected Claim 7 under 35 U.S.C. §112, 12, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. More specifically, the Examiner argued that Claim 7 should be phrased to define a further step from claim 1 not a different process which producing ethylbenzene or styrene. Withdrawal of the respective rejection is respectfully solicited.

As further emphasized in the revised version of Claim 7 as herewith presented, the respective process encompasses a step in addition to and following the steps of Claim 1. Moreover, the additional step set forth in Claim 7 provides that the 4-vinylcyclohexene which is obtained in accordance with the measures set forth in Claim 1, ie. steps (A) to (D) of Claim 7 as herewith presented, is further dehydrogenated to ethylbenzene or to styrene. The Examiner's position that Claim 7 should be directed to a process for the preparation of 4-vinylcyclohexene rather than a process for the preparation of ethylbenzene or styrene is, accordingly, not deemed to be well taken. Withdrawal of the respective rejection is respectfully solicited.

Further, the Examiner reiterated the rejection of Claims 1 to 7 under 35 U.S.C. \$103(a) as being unpatentable in light of the teaching of *Dutcher* (US 2,438,041) when taken in of the disclosure of *Adams* et al. (US 3,161,670).

The Examiner inter alia takes the position that the product of the dehydrogenation step which is addressed in the teaching of Adams et al. does not contain acetylenically unsaturated hydrocarbons and allenes.<sup>2)</sup> The respective position is, however, not supported by the teaching of the reference. In fact Adams et al. does not indicate whether such by-products are present in the product of the dehydrogenation step. The Examiner's position is deemed to be based on hind-sight since knowledge gleaned from applicants' invention is used against applicants' invention.<sup>3)</sup> A hindsight reconstruction of the

<sup>2)</sup> Page 4, lines 1 to 3, of the Office action.

<sup>3)</sup> see Gore & Assocs., Inc. v. Garlock, Inc., 721 F.2d 1540, 1553, 230 USPQ 303 312-313 (Fed. Cir. 1983): "To imbue one of ordinary skill in the art with the knowledge of the invention in suit, when no prior art reference or references of record convey or suggest that knowledge, is to fall victim to the insidious effect of a hindsight syndrome wherein which only the inventor taught is used against the teacher."

Serial No. 10/501,876

WALSDORFF et al.

PF++53257

claimed invention wherein knowledge which is only available from the disclosure of the claimed invention is used to select particular elements from the disclosure of the prior art is, however, impermissible in a determination under Section 103.4) It is well established that obviousness of a claimed invention cannot be predicated on what is unknown.5)

The Examiner further argued that it would have been obvious to a person of ordinary skill to employ the products obtained in accordance with the procedure of Adams et al. in the process of Dutcher "since it is expected that using any butadiene feed would yield similar results."6) It is respectfully urged that the Examiner's respective position is in error. Applicant herewith submit a copy of an article by R. S. Dixit and C. B. Murchison, of Dow Chemical Company, "Crude Butadiene to Styrene Process", which was prepared for presentation at the Sixth Annual Ethylene Producers Conference on April 20, 1994. The article clearly states that C4 streams containing butadiene from crackers are contaminated with C4 acetylenes, and that C4 acetylenes strongly adsorb on Cu catalyst and significantly inhibit the subsequent dimerization reaction. 7) The respective article therefore corroborates that a person of ordinary skill in the pertinent technology could not reasonably expect that "any butadiene feed would yield similar results" as the Examiner would have it. The respective article further emphasizes that it was well known in the pertinent art that butadiene had to meet certain purity requirements in order to be suitable as a starting material in the preparation of 4-vinylcyclohexene, ethylbenzene and styrene.8) The rationale underlying the Examiner's respective argument is, therefore, clearly in error.

In light of the foregoing and the enclosed it is therefore respectfully urged that the teaching of **Dutcher** and the disclosure of **Adams et al.** are insufficient to establish that applicants' invention

<sup>4)</sup> Cf. Interconnect Planning Corp. v. Feil, 774 F.2d 1132, 227 USPQ 543 (Fed. Cir. 1985); Loctite Corp. v. Ultraseal Ltd., 781 F.2d 861, 228 USPQ 90 (Fed. Cir. 1985); In re Fine, 837 F.2d 1071, 5 USPQ2d 1596 (Fed. Cir. 1988); In re Gorman, 933 F.2d 982, 18 USPQ2d 1885 (Fed. Cir. 1991).

<sup>5)</sup> Cf. In re Adams, 356 F.2d 998, 148 USPQ 742 (CCPA 1966); In re Spormann, 363 F.2d 444, 150 USPQ 449 (CCPA 1966); In re Shetty, 566 F.2d 81, 195 USPQ 753 (CCPA 1977); In re Newell, 891 F.2d 899, 13 USPQ2d 1248 (Fed. Cir. 1989); In re Rijckaert, 9 F.3d 1531, 28 USPQ2d 1955 (Fed. Cir. 1993).

<sup>6)</sup> Page 3, lines 19 to 22, of the Office action.

<sup>7)</sup> Cf. "Process Overview", paragraph bridging page 120 and 121, of Dimit at al.

<sup>8)</sup> Cf. applicants' respective remarks in the paper dated March 13, 2006, which is herewith incorporated by reference,

## **BEST AVAILABLE COPY**

Serial No. 10/501,876

WALSDORFF et al.

PF++53257

is unpatentable under Section 103(a). As explained in MPEP \$2143, three basic criteria have to be met in order to establish a prima facie case of obviousness:

- (1) There must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine the reference teachings,
- (2) there must be a reasonable expectation of success, and
- (3) the prior art reference or the combined references must teach or suggest all of the claim limitations.

Additionally, the teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art and cannot be based on the applicant's disclosure. Also, the level of skill in the art cannot be relied upon to provide the suggestion to combine references. At least the first and the second of those criteria are not met. Neither the references themselves nor the knowledge which was generally available to one of ordinary skill in the art provides for the suggestion or motivation which is necessary to combine the references since, as pointed out previously and reiterated in the foregoing, a person of ordinary skill could not reasonably expect that any butadiene containing product was equally suitable as starting material in the process of Dutcher. For the same reason, the reasonable expectation of success is not found in the prior art.

It is therefore respectfully requested that the rejection of Claims 1 to 7 under 53 U.S.C. §103(a) based on the teaching of Dutcher and the disclosure of Adams et al. be withdrawn. Favorable action is respectfully solicited.

#### REQUEST FOR EXTENSION OF TIME:

It is respectfully requested that a one month extension of time be granted in this case. The respective \$120.00 fee is paid by credit card (Form PTO-2038 enclosed).

<sup>9)</sup> In re Vaeck, 947 F.2d 488, 20 USPQ2d 1438, 1442 (Fed. Cir. 1991).

<sup>10)</sup> Al-site Corp. v. VSI Int'l Inc., 174 F.3d 1308, 50 USPQ2d 1161, 1171 (Fed. Cir. 1999).

Serial No. 10/501,876

WALSDORFF et al.

PF++53257

Please charge any shortage in fees due in connection with the filing of this paper, including Extension of Time fees, to Deposit Account No. 14.1437. Please credit any excess fees to such deposit account.

Respectfully submitted,

NOVAK DRUCE DELUCA & QUIGG

Marvin A. Motsenbocker

Reg. No. 36,614

Customer No.: 26474 1300 Eye Street, N.W. Suite 400 East Tower Washington, D.C. 20005 (202) 659-0100

Encl.: CLAIM AMENDMENTS (Appendix I)

R. S. Dixit and C. B. Murchison, "Crude Butadiene to Styrene Process", pages 116 to 133 (AIChE 1994)

MAM/BAS

Fax sent by : 2026590105 NDDQ LLP 08-21-06 19:33 Pg: 7/2

## BEST AVAILABLE COPY

Serial No. 10/501,876

WALSDORFF et al.

DP4453257

#### APPENDIX I:

#### CLAIM AMENDMENTS:

Kindly amend Claim 7 as indicated in the following listing of the claims:

- (previously presented) A process for preparing 4-vinylcyclohexene, which comprises the steps
  - (A) providing an n-butane-containing feed gas stream,
  - (B) feeding the n-butane-containing feed gas stream into at least one dehydrogenation zone and dehydrogenating n-butane to butadiene to give a product stream comprising butadiene, n-butane, possibly 1-butene and 2-butene and possibly water vapor and other secondary constituents, said product stream not containing any significant amounts of acetylenically unsaturated hydrocarbons or allenes,
  - (C) feeding the product stream from dehydrogenation, without prior partial hydrogenation of said product stream, and if appropriate after separating off water vapor and secondary constituents, into a dimerization zone and catalytically dimerizing butadiene to give a product stream comprising 4-vinylcyclohexene, n-butane and possibly 1-butene, 2-butene and unreacted butadiene, and
  - (D) separating off 4-vinylcyclohexene from the product stream from the dimerization and recirculating n-butane and possibly 1-butene, 2-butene and unreacted butadiene to the dehydrogenation zone.
- 2. (original) A process as claimed in claim 1, wherein the provision of the n-butane-containing dehydrogenation feed stream comprises the steps
  - (A1) providing a liquefied petroleum gas (LPG) stream;
  - (A2) separating off propane and, if appropriate, methane, ethane and pentanes from the LPG stream to give a stream comprising butanes,
  - (A3) separating off isobutane from the stream comprising butanes to give the n-butane-containing feed gas stream and, if desired, isomerizing the isobutane which has been separated off to give an n-butane/isobutane mixture and recirculating the n-butane/isobutane mixture to the isobutane separation step.

Serial No. 10/501,876

WALSDORFF et al.

PF++53257

- 3. (previously presented) A process as claimed in claim 1, wherein the dehydrogenation of n-butane to butadiene is carried out as an autothermal catalytic dehydrogenation.
- 4. (previously presented) A process as claimed in claim 1, wherein the dehydrogenation of n-butane to butadiene comprises the steps
  - (B1) feeding the n-butane-containing feed gas stream into a first dehydrogenation zone and catalytically, nonoxidatively dehydrogenating n-butane to 1-butene, 2-butene and possibly butadiene to give a product gas stream comprising butadiene, n-butane, 1-butene, 2-butene and possibly secondary constituents.
  - (B2) feeding the product gas stream comprising n-butane, 1-butene, 2-butene, possibly butadiene and possibly secondary constituents into a second dehydrogenation zone and oxidatively dehydrogenating 1-butene and 2-butene to butadiene to give a product gas stream comprising butadiene, n-butane, water vapor and possibly secondary constituents.
- 5. (original) A process as claimed in claim 4, wherein the catalytic, nonoxidative dehydrogenation of n-butane to 1-butene, 2-butene and butadiene is carried out as an autothermal dehydrogenation.
- 6. (previously presented) A process as claimed in claim 1, wherein water vapor and secondary constituents from the group consisting of hydrogen, carbon monoxide, carbon dioxide, nitrogen, methane, ethane, ethene, propane and propene are separated off from the product stream from the dehydrogenation prior to the dimerization.
- (currently amended) A process for preparing ethylbenzene or styrene which comprises:
  - firstly preparing 4-vinylcyclohexene in accordance with the a process defined in claim 1, comprising
  - (A) providing an n-butane-containing feed gas stream,
  - (B) feeding the n-butane-containing feed gas stream into at least one dehydrogenation zone and dehydrogenating n-butane to butadiene to give a product stream comprising butadiene n-butane, possibly 1-butene and 2-butene and possibly water vapor and other secondary constituents, said product stream not containing any significant amounts of acetylenically unsaturated hydrogarbons or allenes,

## BEST AVAILABLE COPY

Serial No. 10/501,876

WALSDORFF et al.

PF++53257

- (C) feeding the product stream from dehydrogenation, without prior partial hydrogenation of said product stream, and if appropriate after separating off water vapor and secondary constituents, into a dimerization zone and catalytically dimerizing butadiene to give a product stream comprising 4-vi-nylcyclohexene, n-butane and possibly 1-butene, 2-butene and unreacted butadiene, and
- (D) separating off 4-vinylcyclohexene from the product stream from the dimerization and recirculating n-butane and possibly 1-butene. 2-butene and unreacted butadiene to the dehydrogenation zone.

and subsequently

- (E) feeding the 4-vinylcyclohexene into a further dehydrogenation zone and catalytically dehydrogenating it to ethylbenzene or oxidatively dehydrogenating it in the presence of oxygen to give styrene.
- 8. (previously presented) A process for preparing styrene comprising the steps
  - (A) providing an n-butane-containing feed gas stream,
  - (B') feeding the n-butane-containing feed gas stream and a 4-vinylcyclohexene-containing gas stream into a dehydrogenation
    zone and jointly dehydrogenating n-butane and 4-vinylcyclohexene in the presence of oxygen to give a product stream
    comprising styrene, butadiene, n-butane, 1-butene, 2-butene,
    possibly ethylbenzene and further secondary constituents,
  - (C') separating off styrene and, if applicable, ethylbenzene and further high-boiling secondary constituents from the product stream from the dehydrogenation,
  - (D') feeding the stream comprising butadiene, n-butane, 1-butene and 2-butene into a dimerization zone and catalytically dimerizing butadiene to give a product stream comprising 4-vi-nylcyclohexene, n-butane, 1-butene, 2-butene and possibly unreacted butadiene,
  - (E') isolating the 4-vinylcyclohexene-containing gas stream from the product stream from the dimerization and feeding it into the dehydrogenation zone.
- 9. (original) A process as claimed in claim 8, wherein the joint dehydrogenation of n-butane and 4-vinylcyclohexene is carried out in the presence of a dehydrogenation catalyst comprising a noble

Fax sent by : 2026590105 NDDQ LLP 08-21-06 19:34 Pg: 10/2

## **BEST AVAILABLE COPY**

Serial No. 10/501,876

WALSDORFF et al.

PP++53257

metal of transition group VIII together with, if desired, one or more elements of main groups I and/or II, one or more elements of main group III including the lanthanides and actinides and/or one or more elements of main groups III and/or IV on a support.

Volume 3

#### **BEST AVAILABLE COPY**

## Proceedings

# 6TH ETHYLENE PRODUCERS' CONFERENCE

Published by the American Institute of Chemical Engineers 345 East 47th Street, New York, NY 10017 © 1994 AIChE

Session and Paper Number: 22 f

## BEST AVAILABLE COPY

## Crude Butadiene to Styrene Process

Ravi S. Dixit and Craig B. Murchison

The Dow Chemical Company 1776 Bldg. Midland, MI 48674

Prepared for Presentation at

AIChE 1994 Spring National Meeting Atlanta, April 17 - 21, 1994

Sixth Annual Ethylene Producers Conference Technology for Application in Ethylene Plant

April 20, 1994

AIChE shall not be responsible for statements or opinions contained in papers or printed in its publications

## Crude Butadiene to Styrene Process

## BEST AVAILABLE COPY

#### Introduction

One of the natural by-products of ethylene manufacture is a mixture of C4's containing butadiene, butenes and butane. This C4 stream is the predominant feed stock for producing pure butadiene by an extraction process. Currently more than 80% of the worlds butadiene is made from crude C4's and the rest from "on-purpose" dehydrogenation of butane and butenes. The demand growth for ethylene far exceeds that for butadiene resulting in a world wide surplus of butadiene. Production of crude butadiene during ethylene manufacturing is forecast to increase at an average rate of 4.1 percent from 1992 to 1998 [1]. Analysis done by CMAI indicates that the need to destroy crude butadiene will increase from 760,000 tons in 1993 to 1.36 million tons in 1998. This represents an average rate of growth for the destruction of crude butadiene of 11.7 percent worldwide. If the growth rate and rate of destruction for crude butadiene are considered, it indicates that crude butadiene is being produced in olefin plants at a rate that is 28 percent greater than it is consumed. It is important that a viable and profitable longterm solution be found to handle the global butadiene surplus.

The ethylene producer has a number of options available to process the crude C4 stream if the market price does not justify isolation of the pure butadiene. The first option is recycle the crude C4 stream back to the ethylene cracker and co-crack with fresh feed. This is an often used, low capital solution to handle surplus butadiene that requires minimal investment but results in a poor

yield with high coke formation. A second option that has become popular in the last few years has been the partial or complete hydrogenation of the butadiene and butenes in the crude C4 stream. Partial or selective hydrogenation is preferred when there is a market for iso-butene which finds use in MTBE manufacture. Full hydrogenation is used when cracker feed stock is limited, there is excess hydrogen and no cost effective outlets exist for butenes. Full hydrogenation produces butanes that are excellent cracker feed stock. Both selective and full hydrogenation require low to moderate capital expenditure. Both of these options are currently being practiced to remove excess butadiene from the market.

The crude C4 to styrene process developed by Dow offers an attractive, high value alternative to an olefins producer. This process selectively upgrades butadiene in C4 streams to styrene monomer and produces raffinate-1 as a by-product. This technology has been extensively researched at the lab-scale, mini-plant and pilot plant scale to evaluate catalyst and engineering parameters. The process is current being operated at the 18 - 40 lb/hr scale in a Dow Texas pilot plant.

#### **Process Overview**

The schematic of the crude butadiene to styrene process is shown in Figure 1.

The first step involves the mild hydrogenation of the ethylene plant crude C4 stream to remove C4 acetylenes. Acetylenes adsorb strongly on Cu catalysts and significantly inhibit the subsequent dimerization reaction. At this point

the treated C4 stream is passed over a Dow patented copper loaded zeolite catalyst at approximately 100 °C that selectively cyclo-dimerizes butadiene to 4-vinyl-1-cyclohexene (4-VCH). The unreacted C4's can then be separated from the 4-VCH by a simple flash. This second step acts as a reactive separation of butadiene from the crude C4 stream and could be used as a method to isolate butadiene since 4-VCH readily decomposes back to butadiene when heated to about 500 °C. The catalytic cyclo-dimerization is well known in the chemical literature [2-5]. Our contribution is the synthesis of a reasonably stable, regenerable, high activity catalyst and reactor design that allows this to be a practical process [6]. In the present case the 4-VCH made in the dimerization step is then oxidized at about 400 °C over a Dow proprietary oxide catalyst to styrene monomer at greater than 90% yield. Our contribution is a stable, very easily regenerated catalyst and a reactor, process design that results in a practical process. The process has sufficient flexibility and can handle crude C4 streams from a variety of ethylene producers regardless of the feed stock used for cracking.

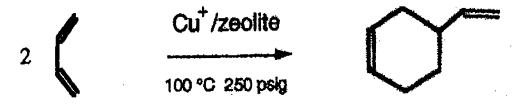
## **Butadiene Dimerization Process**

The dimerization process is carried out in liquid phase over a copper on zeolite catalyst at 100 °C and 250 psig pressure.

NDDQ LLP

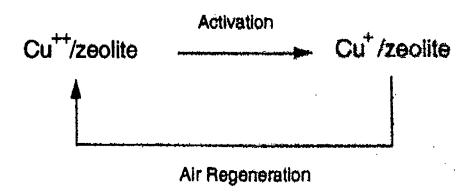
08-21-06 19:35

Pg: 16/28



 $\Delta H = -18 \text{ kcal/mol butadiene}$ 

Butadiene conversion ≥ 90% VCH selectivity ≥ 99%



High pressure is required mainly to keep the reactants in a liquid phase that gives longer catalyst lifetime. The catalyst is inert to all C4 components such as butane, 1-butene, 2-butenes and iso-butene, except 1,3 butadiene. The selectivity to 4-VCH is greater than 99%. The catalyst is activated prior to reaction by olefin reduction such as with the butenes. Under reaction conditions the catalyst shows slow deactivation that is a function of temperature and time on stream. Periodically the catalyst must undergo a "coke" burn off where temperatures are allowed to rise to a maximum of 350°C. The catalyst can be completely regenerated to its initial activity and

Crude Butadiene to Styrene Process

AIChE April 20, 1994

NDDQ LLP

08-21-06 19:36

Pg: 17/28

selectivity levels. Catalyst performance has been demonstrated in a 30 foot show tube reactor. Multiple activation and regeneration cycles with over 2000 hours of on-stream performance has been demonstrated at the 60% conversion level. A kinetic model has been developed using SimuSolv<sup>TM</sup> and is shown in Table 1. This kinetic model is based on a mechanism involving associative adsorption of two butadiene molecules on an active site. It accounts for product inhibition by 4-VCH and moderately strong adsorption of butadiene and iso-butene on the catalyst surface.

Table 1. Kinetic Model for Butadiene Dimerization

Dimerization Kinetic Model
$$-r_{BD} = \frac{a k_0 e^{\frac{E_r}{RT}} C_{BD}^2}{(1 + K_{BD}C_{BD}^2 + K_{VCH}C_{VCH} + K_{CA}C_{CA}^2)}$$

Catalyst deactivation studies showed that deactivation is independent of feed or product concentrations and just a function of temperature and time on stream. The nominal deactivation model is given in Table 2.

TM SimuSolv is a Trademark of The Dow Chemical Company.

NDDQ LLP

M8-21-M6 19:36

Pa: 18/28

Table 2. Deactivation Kinetic Model for Dimerization Catalyst

Deactivation Kinetic Model
$$-\frac{da}{dt} = k_{d0} e^{-\frac{E_d}{RT}} a$$

Due to this slow deactivation the reactor temperature needs to be continuously increased to result in constant butadiene conversion from the reactor. At about 130 °C the deactivation rate is currently judged to be excessive and the catalyst is oxidatively regenerated. An optimization procedure using calculus of variations was applied to develop an optimal temperature policy for the dimerization reactor. A typical temperature policy, shown in Figure 2, indicates that the reactor can be run over 800 hours with constant conversion before requiring catalyst regeneration. Time between regeneration can be increased by changing the operating conditions. Stable catalyst performance is expected over 1 - 2 months of continuous operation without regeneration.

#### VCH Oxidation Process

The second step in the C4 to styrene monomer process is oxidative dehydrogenation of vinylcyclohexene to styrene monomer. The 4-VCH is

NDDQ LLP

08-21-06 19:36

Pg: 19/28

oxidized with oxygen using a Dow proprietary catalyst and steam as a diluent. The reaction conditions are approximately 400 °C and 75 psig.

 $\Delta H = -96 \text{ kcal/mol}$ 

 $\Delta G = -118 \text{ kcal/mol}$ 

VCH conversion ≥ 90% Styrene selectivity ≥ 92%

The typical conversion of 4-VCH is 90% with a styrene selectivity of 92% plus 1-2% selectivity to ethyl benzene. Reaction by-products are benzoic acid, benzaldehyde and CO<sub>2</sub>. Due to a slow deactivation and/or process upsets the catalyst needs to be occasionally regenerated. Surprisingly the catalyst will rapidly regenerate by just curtailing the 4-VCH feed while continuing the steam and oxygen feed at the reaction temperature. The nominal kinetic model that describes the 4-VCH oxidation reaction is given in Table 3.

NDDQ LLP

08-21-06 19:36

Pg: 20/28

## Table 3. Kinetic Model for VCH Oxidation

VCH Oxidation Kinetic Model
$$-r_{VCH} = \frac{k_0 e^{\frac{E_r}{RT}} P_Q^{0.5} P_{VCH}}{(1 + K_e P_{VCH})}$$

#### **Process Description**

The schematic of the C4 to styrene process is shown in Figure 1. The dimerization reaction is carried out in a multi-tubular fixed-bed reactor packed with catalyst. The reactor effluent is sent to a C4-VCH separation tower. The raffinate-1 stream from the tower overhead contains less than 10% butadiene. It can be recycled, processed further to remove butadiene or co-cracked.

A reactor model was developed using SimuSolv and process simulations were done using ASPEN PLUS<sup>TM</sup>.

The 4-VCH from the dimerization process is vaporized, mixed with steam and oxygen and fed to a multi-tubular fixed-bed reactor. The reactor is cooled on the shell-side using a molten salt heat transfer system that removes the

TM ASPEN PLUS is a Registered Trademark of Aspen Technology, Inc., Cambridge, MA.

NDDQ LLP

08-21-06 19:37

Pa: 21/28

exothermic heat of reaction. Appropriate design of the heat exchanger network is used to maximize heat recovery from the reactor effluent. The reactor effluent is then sent to the crude styrene recovery section.

In the crude styrene recovery section, non-condensables and water are removed from an organic stream that contains predominantly styrene monomer. The organic phase is passed over alumina columns to remove oxygenated species before being sent to the finishing section. The crude styrene then is fed to the styrene finishing section where pure styrene, ethyl benzene and 4-VCH are recovered. The 4-VCH is recycled back to the reactor section.

#### **Process Economics**

The amount of crude C4 available at typical ethylene production sites ranges from 300 MM to 700 MM pounds per year. A crude butadiene to styrene plant consistent with this C4 capacity would yield about 150 MM to 300 MM pounds per year styrene monomer. An economic comparison was done for 150 and 300 MM pounds per year C4 to styrene monomer plant located at US Gulf coast relative to a 300 MM pound/yr conventional plant from ethylene and benzene. The relative economics of a world scale 1000 MM lb/yr conventional plant is also shown for reference. The relative economics are shown below in Table 4.

NDDQ LLP

08-21-06 19:37

Dα· 22/28

Table 4. Economics of C4 to Styrene Relative to Conventional 300

MM lb/yr

(1996 \$, US Gulf Coast)

	Ethylene /Benzene Conven.	Ethylene /Benzene Conven.	C4 to Styrene	C4 to Styrene
Capacity	300 MM	1000 M M	150 MM	300 MM
Capital/lb*	0 ¢	-3.1 ¢	9.2 €	-4.1 ¢
Cost/lb**	0 ¢	-3.4 ¢	-6.8 ¢	-9.7 ¢
Cost + 15%	0¢	-3.8 ¢	-5.4 ¢	-10.3 €

<sup>\*</sup> Includes ethylene backup capital

Feed and product values of crude C4 = 11.2¢/lb, ethylene = 20.5¢/lb, benzene = 17.5¢/lb, and raffinate-1 = 12.9¢/lb are used in the calculation. These cost figures are for year 1996 and represent projected estimates. These calculations show a significant advantage for the crude C4 plant relative to conventional styrene. Surprisingly, even the very small 150 MM lb/yr crude C4 plant is competitive with conventional technology.

In summary, Table 4 shows that the styrene monomer cost plus 15% return on capital for the crude C4 case is 10.3 ¢/lb less at the 300 MM lb/yr scale than

<sup>\*\*</sup> Raffinate-1 sold

Fax sent by : 2026590105

NDDQ LLP

08-21-06 19:37

Pg: 23/28

the conventional process at the same capacity. The cost plus 15% for the crude C4 process is also 6.5 ¢/lb less than the conventional at the 1000 MM lb/yr world scale plant

#### Conclusions

Dow has developed a two-step process to produce styrene monomer from crude C4 streams. The first step involves liquid phase dimerization of butadiene contained in the C4 stream to vinylcyclohexene. A Dow proprietary Cu/zeolite catalyst is used which gives 100 % selectivity to vinylcyclohexene. The second step converts vinylcyclohexene to styrene monomer using oxidative dehydrogenation over a Dow proprietary catalyst. This catalyst gives 90 % conversion of vinylcyclohexene with a greater than 92% selectivity to styrene monomer. The overall yield of styrene from butadiene is greater than 90%. This process has been demonstrated on a pilot plant scale.

The Dow C4 to styrene process offers an alternative to C4 co-cracking and C4 hydrogenation. Attractive grass-root economics are obtained at significantly less than typical world scale capacity which is very significant for this mature, slow growth commodity monomer. The process has sufficient flexibility and can tolerate crude C4 streams from a variety of ethylene plants regardless of the feed stock used for cracking. It offers ethylene producers a cost effective alternative for optimizing the plant profitability.

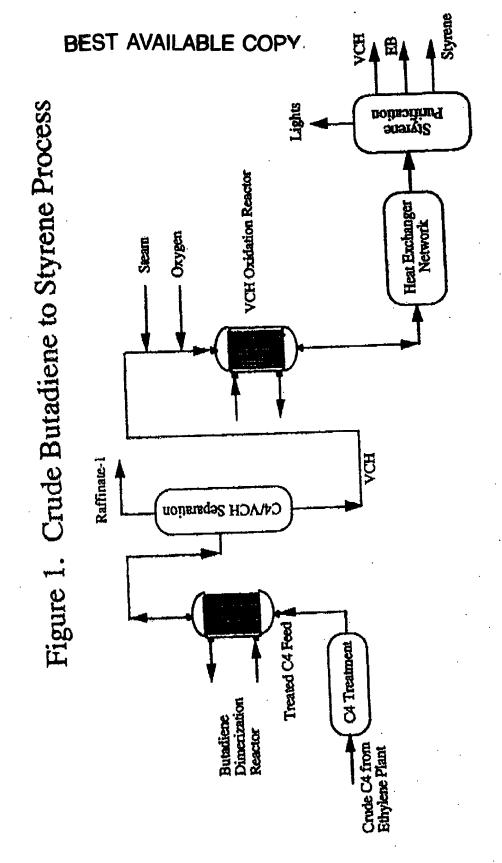
AICHE April 20, 1994

#### Acknowledgments

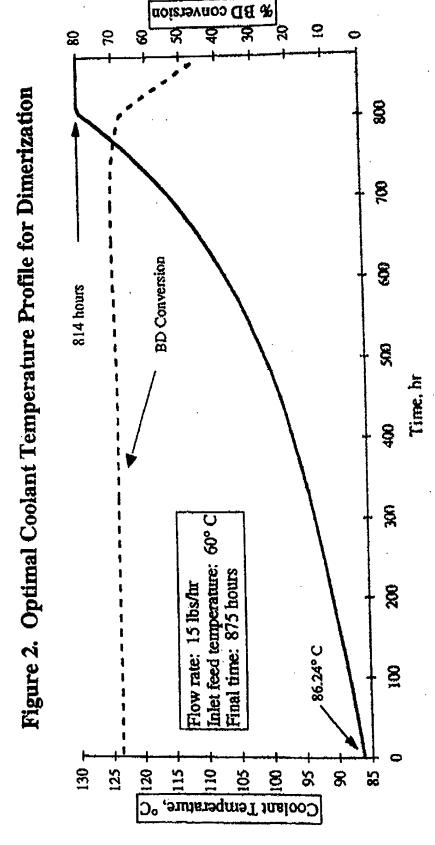
## BEST AVAILABLE COPY

We would like to acknowledge the contributions of a large number of individuals whose creative work resulted in this technology. The principal scientist and engineers are R. Diesen, K. Burdett, S. King, F. Stone, D. Hucul, M. Smith, R. Pierce, L. Tau, B. Sierra and S. Krietenstein of Dow's Central Research and Texas Hydrocarbons Laboratories. Their leadership and diligent work is particularly appreciated.

NDDQ LLP



AICHE April 20, 1994



PAGE 26/28 \* RCVD AT 8/21/2006 8:34:14 PM [Eastern Daylight Time] \* SVR:USPTO-EFXRF-1/1 \* DNIS:2738300 \* CSID:2026590105 \* DURATION (mm-ss):08-18

#### Literature Cited

## **BEST AVAILABLE COPY**

- [1] "World Butadiene Analysis 1993", Chemical Market Associates, Inc., Houston, January 1994.
- [2] Renger, P., F. Janowski, F. Wolf and E. Jahn, Z. Chem., 19(5), 194.
- [3] Dessau, R. M., J. Chem. Soc. Chem. Commun. 1986, 1167.
- [4] Downing, R. S., J. van Amstel and A. Jostra, U.S. Patent 4,125,483, Nov. 14, 1978.
- [5] Maxwell, I. E. and E. Drent, J. Catal., 1976, 41, 412.
- [6] U.S. Patent 5,196,621, March 23, 1993, The Dow Chemical Co.